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Raman Shift of Stressed Diamond Anvils: Pressure Calibration and Culet Geometry Dependence

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Abstract:

The pressure dependence of the Raman shift of diamond for highly stressed anvils at the diamond-anvil sample interface has been measured for different culet shapes up to 180 GPa at ambient temperature. By using hydrogen samples, which constitute both a quasi-hydrostatic medium and a sensitive pressure sensor, some of the effects of culet and tip size have been determined. We propose that the divergent results in the literature can be partly ascribed to different anvil geometries. Experiments show increasing second order dependence of the diamond Raman shift with pressure for decreasing tip size. This is an important consideration when using the diamond anvils as a pressure sensor.

Introduction:

In recent years it has been demonstrated that the Raman shift of the diamond tip at the sample-culet interface can serve as an in-situ pressure sensor at very high pressures [1-5] and be a useful alternative to the ruby luminescence standard.[6-7] This newer technique has the benefit of always having in place a pressure sensor very near the sample. Additionally, the quantum efficiency of the Raman Effect for diamond does not suffer as appreciably as ruby luminescence above 140 GPa.[8-9] However, just as with ruby, the many calibration curves of the pressure dependence of the diamond Raman shift are somewhat divergent. In this paper we will show that some of the discrepancies can be attributed to culet shape. Furthermore, since these are stressed anvil measurements, the sample stiffness and lack of hydrostaticity can also contribute to variations in the Raman shift.

The reports for the Raman shift of diamond depend on the ability to accurately determine the pressure when at ultrahigh pressures. Both the merits and problems of choosing either x-ray diffraction of a standard such as platinum, the ruby luminescence technique or the Raman shift of hydrogen (used in this paper) to calibrate the diamond Raman shift are numerous and space limitations prevent a detailed discussion. Applying these techniques has resulted in several different calibrations using a variety of functional forms.[2-5]

The earliest published report detailing the use of the diamond anvil for pressure measurements went up to 30 GPa.[10] However, it has become increasingly common for diamond-anvil-cell experiments to exceed a megabar. Typically, the ruby standard is

used for the in-situ pressure measurement and has been extensively studied.[6-9,11-15] Given the ruby's intense luminescence below 60 GPa, it is not surprising that this has become a nearly universal spectroscopic pressure sensor; thus a number of different calibrations have been published pertaining to its use. Below a megabar, 100 GPa, there is some divergence among the various formulae which are typically fit to the equation:

$$P = \frac{A}{B}\left[\left(\lambda/\lambda_0\right)^B - 1\right]$$

where λ is the ruby R_1 line at pressure and λ_0=694.28 nm at ambient temperature. Since its initial calibration,[7] a number of experimental attempts have been made to determine the values for A and B.[12] Recently, a detailed comparison and analysis has been made [13] and experiments yielded the values A=1876±6.7 GPa and B=10.71±0.14 for quasi-hydrostatic samples. However, for approximately two decades it has been common to use the values of A =1904 GPa and B =7.665 for very high static pressures.[14]

The best reason to use diamond as the pressure sensor in spectroscopic experiments at ultrahigh pressures is that it becomes increasingly difficult to excite ruby and detect its luminescence. The electronic levels associated with the optical absorption necessary to excite ruby increase in energy with pressure whereas the energy levels associated with emission decrease in energy. As a result, the excitation efficiency (and, therefore, the quantum efficiency) of ruby luminescence rapidly decreases at very high pressures for any given excitation source: which has typically been the argon ion laser. Two analyses of the best wavelength for excitation have been made,[9,15] but the quantum efficiency is still very low above 150 GPa.

Experiment:

Samples of high purity hydrogen were compressed into a membrane diamond anvil cell (MDAC) using a high pressure gas loading system. These samples were confined by a rhenium gasket containing several ruby chips along with hydrogen. All experiments are done at ambient temperature, which is 298 ± 2K. Spectra of ruby luminescence, hydrogen and diamond Raman emission were taken using a 30º backscattering geometry at various pressures up to 180 GPa using 488 nm excitation from a Spectra Physics Stabilite 2017 argon ion laser. Raman spectra were measured with a Spex Triplemate Model 1877 that used a liquid nitrogen cooled CCD array detector from Princeton Instruments. Extensive spatial filtering, which allowed us to image regions smaller than 5μm x 5μm, prevented much of the diamond fluorescence and Raman emission that was not near the diamond-sample interface from reaching the monochromator. The sample pressure was increased by using pressurized helium to apply load to the membrane diamond anvil cell. This permitted finely controlled, nearly uniform and stable pressure changes.

Initially, pressure measurements were made using the ruby luminescence technique taking the values of A and B from Mao et al.[14] This allowed us to directly compare our results for the pressure dependent Raman Shift of hydrogen with those from Mao et al.[16] Above 150 GPa the Raman shift of diamond could be extrapolated to provide an accurate pressure determination. The choice of extrapolating the diamond Raman shift rather than that of hydrogen comes from the observation that the pressure

dependence of diamond appears to be accurately fit to a second order polynomial whereas the Raman shift of hydrogen has been fit to much higher order polynomials.[17] Choosing to extrapolate the pressure dependent Raman shift of either a particular diamond anvil geometry or hydrogen versus ruby luminescence obviously risks a systematic error, but probably no greater than any other alternative pressure sensor to ruby. Once a sufficient number of samples had been analyzed, a fit of the hydrogen Raman data as a function of pressure could be made so that above 50 GPa the Raman shift of hydrogen was deemed the more reliable pressure sensor – especially above 150 GPa.

Diamond anvils are typically, but not necessarily, cut so that the table and culet are in the [001] crystal direction. The diamond Raman shift of three culet shapes was compared; a 300 micron flat, a beveled culet starting at 300 microns with a 75 micron tip (central flat) with a bevel angle of 8.5 degrees, and a culet starting at 400 microns with a 50 micron tip also with a bevel angle of 8.5 degrees. Smaller tips, as expected, require smaller gasket sample holes. Hydrogen is highly compressible, the sample holes typically shrunk to be about 20 to 25% the diameter of the tip at high pressure. The diamonds are natural in origin and are, therefore, composed of 98.9% ^{12}C and 1.1% ^{13}C. All of the diamonds were Type I and selected for low fluorescence and birefringence. A study using isotopically pure ^{12}C diamonds has been done,[18] but is less applicable since most diamonds used for high pressure experiments contain carbon isotopes in their natural abundance.

Results and Discussion:

A graph of the Raman shift of hydrogen at ambient temperature as a function of pressure that includes similar data from an earlier study by Mao et al.[16] for purposes of comparison is shown in figure 1. The results of these two sets of experiments agree extremely well, suggesting that for a given ruby pressure scale the hydrogen Raman shift can be consistently measured between different labs and helps support the use of extrapolating the diamond Raman for pressure measurements. The data taken in our study is less scattered due to the use of a MDAC which can apply load very evenly and avoids the mechanical friction and relaxation of the bolts experienced with a bolt driven piston. Since the goal of this research is to construct a credible calibration of the diamond Raman shift and provide guidance for its use with different anvil geometries, an accurate measurement of the hydrogen Raman shift is vital. Although the pressures above 150 GPa were initially determined by a single anvil geometry, the hydrogen Raman shift serves as our pressure sensor for other anvils.

A typical Raman spectrum of the diamond anvil at the sample culet interface can be seen in figure 2. The smoothed fit is an approximation of the sum of contributions from the diamond fluorescence, the diamond at the sample interface and the diamond anvil out of the plane of focus of the optics. The first derivative of that fit is also shown in the figure. Unlike some earlier studies[3,19] that reported it could observe the splitting of the triply degenerate Raman peak of diamond into a doublet and singlet due to uniaxial stress, especially along the [111] crystal direction,[19] we could only reliably distinguish a single peak in our spectra. This may be due to our use of more fluorescent diamonds.

The center peak position of this single peak was used for the purpose of determining Raman shift pressure dependence. The example shown in figure 2, which was taken at 140 GPa, corresponds almost exactly to that made for a study of natural diamond in helium.[20] Although the purpose of that study was to determine the Raman shift of diamond under near hydrostatic conditions, the Raman spectrum which appears in figure 1 of reference 20 also contains the contribution from the anvil. The peak position of diamond from the anvil in that helium sample corresponds almost exactly with what we measure using hydrogen as a pressurization medium. The divergence in Raman Shift between diamond in a quasi-hydrostatic medium and the anvil tip had been previously observed.[21]

Using the calibrated hydrogen Raman shift; a diamond Raman shift dependence can be measured independent of ruby. There is a maximum in the Raman shift of hydrogen [22] near 25 GPa which limits its use to a minimum of 50 GPa for the calibration of this study. Between 20 and 45 GPa the change in vibration frequency is relatively small and possibly ambiguous, which would lead to a large uncertainty. In figure 3 the Raman shift of diamond at the diamond-sample interface is graphed as a function of hydrogen Raman shift above 50 GPa for two different culet designs. Using this relative Raman shift relationship essentially removes the ruby standard from the pressure measurements. Note that the divergence is only noticeable above a megabar, but that the two culet designs are not the equivalent. If one is to use the Raman shift of the diamond anvil as a pressure sensor at ultrahigh pressures it is vital that as much information be obtained pertaining to that particular anvil-sample pressure dependence.

To reconcile our results with previous experiments one must take into account both the culet design and the sample. This had been suggested in a paper by Eremets[1] which reported no observable variation, but cautioned that the study was not systematic. This is likely the case for many of the other previous reports that do not observe a culet geometry dependence.[3-5] Furthermore, the precision of pressure measurements without a quasihydrostatic medium, which is the case for many of these studies, add to their data scatter. A comparison of our three culet designs versus that of other experiments is shown in figure 4. Differences greater than 10% occur well below 200 GPa. Extrapolations of the curves suggest that a very large error would be introduced if the calibration used for one anvil design were assumed to be universal. This limits the effectiveness of using the diamond anvil as a sensor at ultrahigh pressures if that anvil design had not been carefully calibrated for that particular sample.

Several interesting differences emerge from comparing the different results in the literature with this study. The Raman shift measured for the 300 micron culet having no bevel overlap very closely with that for hydrostatic diamond.[20] This may be due to the fact that a hydrogen sample with a much larger gasket aperture may approximate conditions that are closer to that of quasi-hydrostaticity at low pressures than those samples with a very small tip and commensurately smaller apertures. Clearly, from the graph, the extrapolation of the 300 micron culet data to ultrahigh pressures would yield pressures that are systematically too low.

Consistent with smaller tips having greater second order pressure dependence, the data from Akahama et al. comes from 30 and 35 micron culets.[4] However, their choice of a relatively non-hydrostatic pressure medium makes it difficult to separate out other

possible stress inducing effects on the diamond tip. This data fit is very similar to that from a study done by Popov,[3] which matches our 50 micron tip results up to 120 GPa and then nearly converges with Akahama et al.[5] at much higher pressure. Unfortunately Eremets[1] did not report an equation with his fit to the data, but his results to appear to be consistent with this report. It is much more difficult to reconcile the data from Sun et al.[2] and Vohra et al.[18] between 60 and 200 GPa, since these two reports are the only ones to observe a linear dependence at ultrahigh pressures. In the Sun et al. study, the use of a tungsten gasket, rather than rhenium, is unlikely to be the source of the discrepancy. However, in the Vohra et al. study, the discrepancy between the EoS of copper without a quasihydrostatic medium versus that of the ruby luminescence for pressure determination could lead to a significant calibration error. A table of the pressure dependence of diamond Raman shifts for various culet shapes plus that for quasi-hydrostatic diamond is shown below. All data is fit to the equation:

$\nu\left(cm^{-1}\right) = \nu_0 + aP + bP^2$, where P is in GPa.

	ν_0	a	$b*10^3$
300 micron culet	1332.4(6)	2.709(11)	-0.517
300/75 micron culet	1332.4(6)	2.283(7)	-1.051(28)
400/50 micron culet	1332.4(6)	2.301(7)	-1.702(27)
Reference 4 (30 and 35 micron tips)	1332.5(5)	2.212(2)	-2.085(2)
Reference 20 (hydrostatic diamond)	1333	2.83(1)	-3.65

Conclusion: The Raman shift of the diamond anvil has been used to measure sample pressure in diamond-anvil-cell experiments at very high pressures. However, like ruby, the literature has several equations describing this pressure versus spectral shift relationship that diverge significantly by a megabar. Nonhydrostatic conditions, anvil crystallographic orientation, and culet design can significantly alter this relationship and should be taken into account for any experiments done at ultrahigh pressures. Experiments demonstrate increasing second order dependence in the stressed diamond anvil Raman shift as the tip size decreases.

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Figure Captions:

1) Pressure dependence of the Raman shift of hydrogen at ambient temperature. The open squares are from reference 16 and the open diamonds are data from this study. The line fit through our data is $\nu\,(cm^{-1}) = (-1.039*10^{-2})P^2 - 0.1306*P + 4288$, for $50\ GPa \leq P \leq 180\ GPa$.

2) Raman spectrum of the diamond anvil (400 micron culet with 50 micron flat) for a sample of hydrogen at 140 GPa at the tip. The bold line is the smoothed fit of the data. Lower panel: First derivative of smoothed fit.

3) Raman shift of the diamond tip as a function of the Raman shift of hydrogen. The open diamonds are for culets that are 300 microns in diameter with a 75 micron flat. The open squares are for culets that are 400 microns in diameter with a 50 micron flat.

4) Comparison of various earlier pressure dependent diamond and anvil tip (solid and dashed lines) Raman shift measurements with our (symbols) data. See table 1 for line fit details.

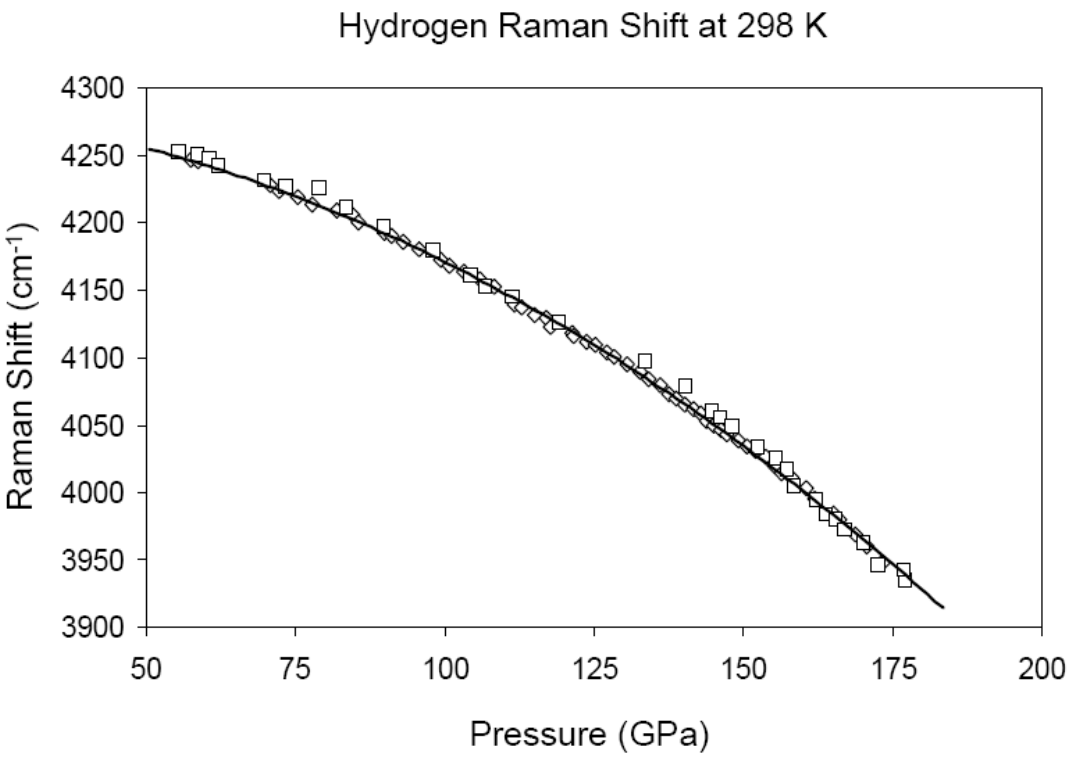
Hydrogen Raman Shift at 298 K
Raman Shift (cm-1)
4300
4250
4200
4150
4100
4050
4000
3950
3900
50
75
100
125
150
175
200
Pressure (GPa)

fig. 1

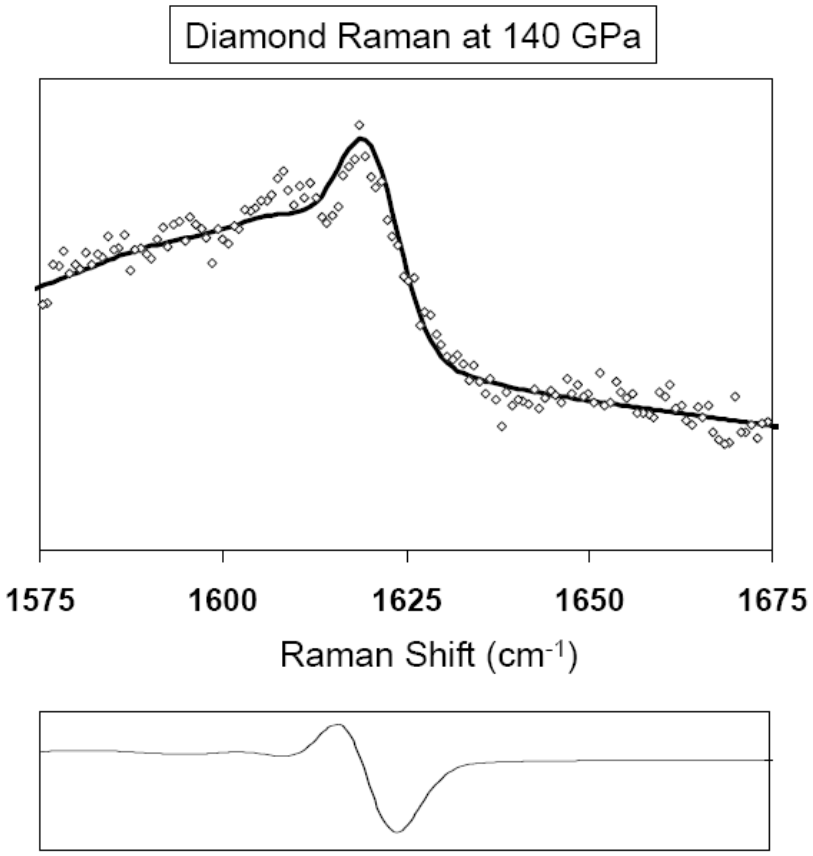
Diamond Raman at 140 GPa
1575
1600
1625
1650
1675
Raman Shift (cm-1)

fig 2

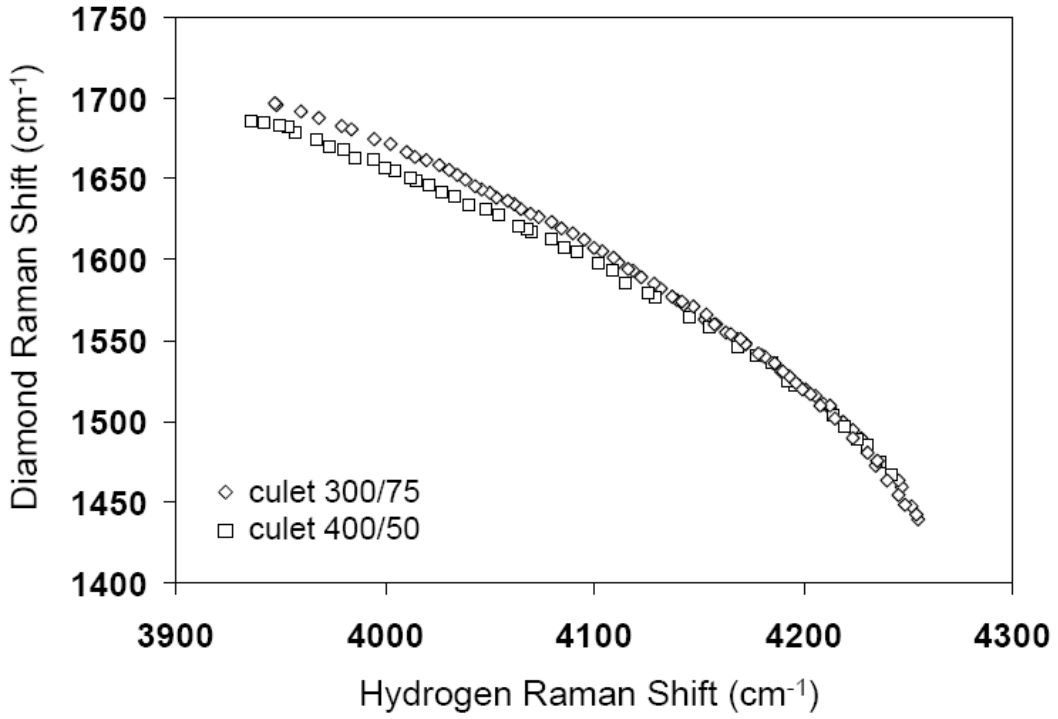
1750
1700
1650
1600
1550
1500
1450
1400
Diamond Raman Shift (cm-1)
culet 300/75
culet 400/50
3900
4000
4100
4200
4300
Hydrogen Raman Shift (cm-1)

fig. 3

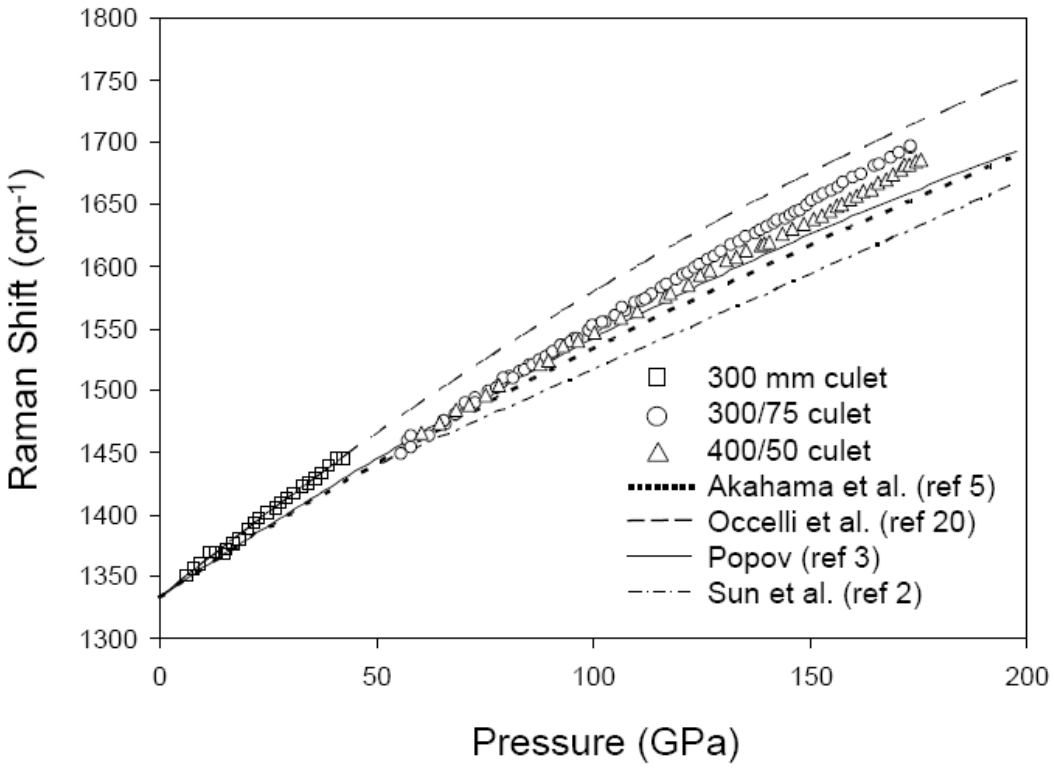
Raman Shift (cm-1)
Pressure (GPa)
1800
1750
1700
1650
1600
1550
1500
1450
1400
1350
1300
0
50
100
150
200
300 mm culet
300/75 culet
400/50 culet
Akahama et al. (ref 5)
Occelli et al. (ref 20)
Popov (ref 3)
Sun et al. (ref 2)

fig. 4